# Relevance of nonadiabatic effects in TiOCl

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**Abstract.** We analyze the effect of the phonon dynamics on a recently proposed model for the uniform-incommensurate transition seen in TiOX compounds. The study is based on a recently developed formalism for nonadiabatic spin-Peierls systems based on bosonization and a mean field RPA approximation for the interchain coupling. To reproduce the measured low temperature spin gap, a spin-phonon coupling quite bigger than the one predicted from an adiabatic approach is required. This high value is compatible with the renormalization of the phonons in the high temperature phase seen in inelastic x-ray experiments. Our theory accounts for the temperature of the incommensurate transition and the value of the incommensurate wave vector at the transition point.

## 1. Introduction

The renewed interest in spin-Peierls (SP) systems arises from the recently characterized compounds TiOX (X = Cl, Br). TiOCl is a quasi-one-dimensional antiferromagnet with strong spin-phonon coupling. Different than the previously studied organic and inorganic SP systems, TiOX has an intermediate incommensurate phase between the dimerized and the uniform ones. Motivated by a phenomenological Landau-Ginzburg calculation [1], we have recently studied a model of Heisenberg chains coupled to phonons [2]. As a simplified phononic model we had taken arrays of harmonic chains inserted in an anisotropic triangular lattice. The transversal elastic coupling arising in this geometry introduces a degeneration of the phonon mode at the zone boundary (ZB). This degeneration induces a linear dependency of the phononic dispersion near the ZB which is different than the usual flat dispersion close to the ZB. We had shown that this difference is at the heart of the fact that TiOX undergoes an instability from the high temperature uniform phase to an incommensurate phase instead of a dimerized one.

In spite of the fact that the transition can be accounted by an adiabatic treatment of the phonons, the temperature scale seems to be strongly renormalized. In fact, by taking the spin-phonon coupling and the bare phonon frequency obtained at the ZB from ab-initio calculations, neither the phononic dispersion measured at $T = 300K$ nor the wave vector of the incommensuration could be reproduced. By increasing the spin-phonon coupling in order to solve the previous problem, the critical temperature turned out to be much bigger than the experimental one [2].

In the present work we investigate the consequences of the inclusion of the dynamics of the phonons. We treat the effective interchain coupling generated by integrating out the phonons within a mean field *random phase approximation* (RPA) framework recently developed [3]. We show that a consistent description of the dimerized phase, the renormalization of the phonons

by their interaction with the magnetism, and the characteristics of the incommensurate-uniform transition are well accounted within this approach.

## 2. The model and its low temperature phase

We consider the model proposed in Ref. [2] for the bilayer of TiOCl. This simplified model included the spin chains coupled to phonons and the elastic springs defined on an anisotropic triangular lattice. Those are the essential ingredients for the incommensurate transition as previously shown [2]. The model is sketched in Fig. 1. Here, we have added a transversal elastic

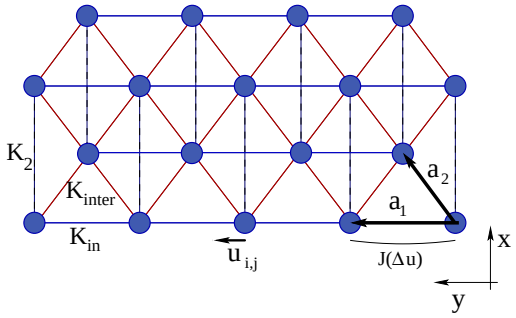


**Figure 1.** Schematic representation of our simplified model. Only Ti atoms are included over the $xy$ plane. $K_{in}$, $K_{inter}$ and $K_2$ are the harmonic force constants acting when two atoms in the same chain, in neighboring chains and in next-nearest neighbor chains respectively move from their equilibrium position. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the base vectors. The coordinate of an atom is given by $\mathbf{R}_{ij} = i\mathbf{a}_1 + j\mathbf{a}_2$.

interaction between ions in second neighbor chains with spring constant $K_2$. Whereas it does not play any role in the adiabatic treatment, we will show that it is essential to account for a finite temperature phase transition in our treatment with nonadiabatic phonons. The Hamiltonian reads

$$\begin{aligned} H &= \sum_{i,j} \frac{P_{i,j}^2}{2m} + \sum_{i,j} \{ \frac{K_{in}}{2}(u_{i,j} - u_{i+1,j})^2 + \frac{K_{inter}}{2} \left[ (u_{i,j} - u_{i,j+1})^2 + (u_{i,j} - u_{i+1,j-1})^2 \right] \\ &+ \frac{K_2}{2}(u_{i,j} - u_{i-1,j+2})^2) \} + \sum_{i,j} [J + \alpha(u_{i,j} - u_{i+1,j})] \, \mathbf{S}_{i,j} \cdot \mathbf{S}_{i+1,j}, \end{aligned}$$

where $P_{i,j}$ is the momentum of the atom $i,j$ (the integer indexes identifying an atom in the Bravais lattice of Fig. 1), $u_{i,j}$ are the displacements from the equilibrium positions along the direction of the magnetic chains, $\mathbf{S}_{i,j}$ are spin-$\frac{1}{2}$ operators with exchange constant $J = J(\Delta u = 0)$ along the y-axis of a non-deformed underlying lattice, $\alpha = (\mathrm{d}J(\Delta u)/\mathrm{d}\Delta u)|_{\Delta u=0}$ is the spin-phonon coupling constant, and $K_{in}$, $K_{inter}$ and $K_2$ are the harmonic force constants as shown in Fig. 1.

We now consider the low temperature dimerized phase. It is customary to integrate out the phononic coordinates by going to a path integral formulation. The generated effective theory contains retarded interactions between spin-spin dimers along the chain and between different ones. Its low energy behavior can be studied by bosonization in similar steps as in Ref. [3]. Furthermore, a mean field treatment of the effective interchain interaction reduces the problem to a one-chain problem. The mean field order parameter is $\epsilon_0(i) \sim (-1)^i (< \mathbf{S}_{i,j} \cdot \mathbf{S}_{i+1,j} > - < \mathbf{S}_{i+1,j} \cdot \mathbf{S}_{i+2,j} >)$ describing the magnetic dimerization along the chains. At low temperatures we expect a uniformly dimerized phase, thus we take $\epsilon_0$ to be position independent. The resulting one-chain bosonized problem corresponds to a massive sine-Gordon theory which can be exactly solved. Solving the mean field equation by minimizing the total energy with respect to $\epsilon_0$, we obtain for the magnetic gap

$$\frac{\Delta}{J} = CF\lambda, \tag{1}$$

with

$$F(K_{in}, K_{inter}, K_2) = 1 - \frac{1}{\sqrt{1 + \frac{K_2}{K_{in}+K_{inter}}}}, \tag{2}$$

which distinguishes our problem from the square lattice geometry. In Eq. (1), $\lambda = \frac{\alpha^2}{J(K_{in}+K_{inter})}$ is the adimensional spin-phonon coupling. Note that $(K_{in} + K_{inter})$ appears in $\lambda$ instead of $K_{in}$ alone because it gives the phononic frequency at $q_y = \pi/b$ for our model. Furthermore, the constant $C = 21.652\beta^2$ is model independent. However, it depends on the nonuniversal constant $\beta$ necessary in the bosonization procedure . We discuss a procedure to fix $\lambda$ independently of the value of this constant.

Let us analyze the form of Eq. (1) for limiting values of $K_2$ . When $K_2 \to 0$, then $\Delta \to 0$, i.e. no gap is present and the system does not have a dimerized phase because no coherent dimerization is fixed by the interchain coupling. This is different than the results of the adiabatic approach and was the reason to include $K_2$ in the model. It can be present from the original microscopic phononic model or it could be generated (at least partially) in the low energy Hamiltonian as an effective interaction. In the opposite limit $K_2 >> K_{in} + K_{inter}$, we have $\Delta/J = C\lambda$ which is the result of the adiabatic approach [3]. Let us fix $\Delta/J$ to their experimental values and look for the spin-phonon coupling in the adiabatic ($\lambda^{ad}$) and nonadiabatic ($\lambda$) calculations. We have $\lambda^{ad}/\lambda = F$ depending on the bare phononic parameters. In the next section we obtain $F \simeq 0.22$ by fitting the renormalized phonons to the ones measured in x-ray experiments at $T = 300K$. Moreover $\lambda^{ad} = 0.58$ has been obtained by ab-initio electronic structure calculations [4]. We obtain $\lambda \simeq 2.6$, thus the nonadiabatic approach requires a bigger spin-phonon coupling to produce the same spin gap. We will check this value in the next section.

Finally, the critical temperature can be obtained as $T_c/J = 0.25342F\lambda$ where $\beta$ has been obtained from the procedure of Ref. [5]. We obtain $T_c = 96K$ which has to be compared with $T_{c1} = 66K$, the dimerized-incommensurate transition temperature. However, our $T_c$ corresponds to the stability limit of the dimerized phase toward an uniform one, and should be taken as an upper limit. In fact, as we have recently shown for the XY model [6], our model will undertake a first order phase transition to an incommensurate phase at a lower temperature than $T_c$. Note that our value for $T_c$ coincides with the experimental value of $T_{c2}$, which corresponds to the uniform-incommensurate transition.

**3. Softening of an incommensurate phonon in the high temperature phase**

In the high temperature uniform phase, the order parameter $\epsilon_0(i)$ vanishes. This is essential to extend the previous approach to the dynamical correlation functions. Indeed, to compare with x-ray scattering data, the dynamical structure factor $S(\mathbf{q}, \omega)$ has to be determined. It is proportional to the phononic retarded Green function $\mathcal{D}^{ret}$. Following the canonical work of Cross and Fisher (CF) [7], we have recently obtained $\mathcal{D}^{ret}$ by RPA *on the spin phonon coupling* [2]. This corresponds to fluctuations over the adiabatic approximation for the phonons. The softening of an incommensurate phonon was obtained, signaling the uniform-incommensurate transition. In order to go beyond this approach to discuss the nonadiabatic effects, we use the result of Ref. [3] where the RPA is taken *on the effective interchain coupling* generated by the integration of the phonons. This follows the same line of reasoning of the previous section. In Fig. 2 we show the evolution with temperature of the dressed phonon frequencies obtained from the position of the peaks of $S(\mathbf{q}, \omega)$. The high temperature limit corresponds to the bare phononic dispersion. The frequency at the ZB, $\sqrt{4(K_{in} + K_{in})/m}$, has been fixed to the one obtained from ab-initio calculations [8] for the degenerate $A_g$, $B_u$ modes at $175cm^{-1}(\sim 22meV)$. The relation between $K_{in}$ and $K_{inter}$ and the value of $K_2$ have been determined by fitting the peaks to the ones measured in inelastic x-ray experiments [9] at $T = 300K$ and the temperature of the incommensurate transition. Our best fit is shown by continuous lines in the figure.

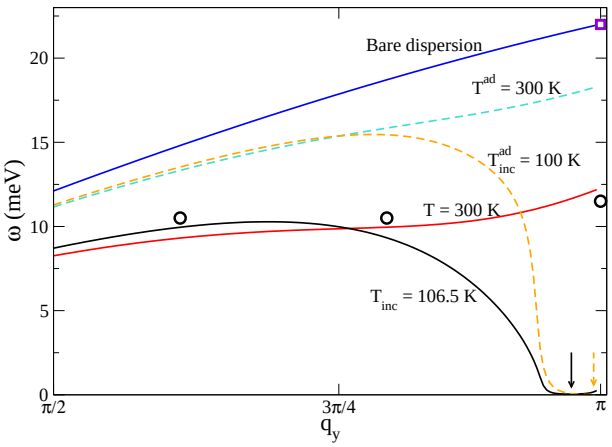


**Figure 2.** Temperature evolution of the dressed phonon frequencies along the $(0, q_y)$ path, at $T \to \infty$, $T = 300K$ and $T_{inc}$. The continuous lines correspond to the nonadiabatic approach while the dashed ones correspond to the adiabatic-CF approach. The arrows signal the incommensurate wave vector at the transition point. The circles show the experimental frequencies at $300K$ [9]. Note that the bare frequencies are the same in both cases but the spin-phonon interaction is different as discussed in the text.

Once the parameters have been fixed, we are able to calculate $F \simeq 0.22$, the value used in the previous section. We also obtain $q_y \simeq 3.05$ for the incommensurate wave vector at the transition temperature which is signaled by the continuous arrow in the figure. This value reproduces very well the one measured by elastic x-ray scattering [9] for the incommensuration in the direction of the magnetic chains. Note that Fig. 2 has been obtained using the $\lambda = 2.6$ obtained from the low temperature phase. If, instead of this value, we use $\lambda^{ad} = 0.58$ extracted from the adiabatic approach, not a good fitting to the measured phonons at $300K$ neither the value of the incommensuration can be obtained. The dashed lines in Fig. 2 show the dressed frequencies obtained from the RPA 'a la' CF, i.e. the adiabatic approach, with the previously fitted phononic parameters and $\lambda^{ad} = 0.58$. We see that not a good fitting is obtained.

In summary, we have analyzed the effects of the inclusion of nonadiabatic phonons on a simple model for TiOCl. We have found that the spin-phonon coupling is strongly renormalized in relation to the one which arises from an adiabatic treatment of the phonons. We used the bare phonon frequency obtained by ab-initio calculations and fitted the elastic spring constants to obtain the experimental phononic frequencies measured at $300K$ by inelastic x-ray scattering. In contrast to the adiabatic treatment, we obtain a good prediction for the uniform-incommensurate transition temperature and for the incommensurate wave vector.

## Acknowledgments

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